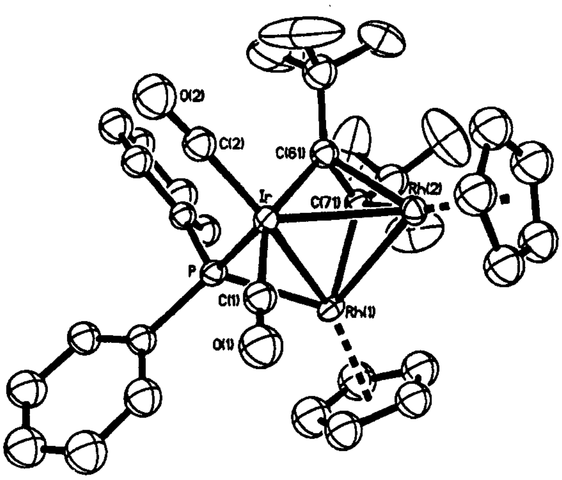

Figure 2. Alternative view of the molecular structure of (η-$C_5H_5)_2Rh_2Ir(\mu$-$PPh_2)(CO)_2(CF_3C_2CF_3)$.

from the calculated Bragg scattering angle at a scan rate of 0.06° s^{-1}. Two standard reflections ((600) and (330)) were monitored every 4 h and showed no significant intensity variation. Intensity data were corrected for Lorentz and polarization effects, and a face-indexed numerical absorption correction was applied.[32] This gave 8014 unique reflections, 5195 of which were considered observed with $\{F_o > 6\sigma(F_o)\}$. The space group $P2_1/c$ was uniquely determined by its systematic absences. A three-dimensional Patterson synthesis revealed the position of the iridium atom. A subsequent difference Fourier synthesis phased with this atom located positions of the two rhodium atoms, along with the phosphorus atom. Successive difference Fourier calculations using SHELX-76[32] readily revealed the remainder of the molecular skeleton. Neutral scattering factors were employed for all atoms and were corrected for anomalous dispersion.[33] Anisotropic thermal parameters were introduced for Ir, Rh, and P atoms. Isotropic temperature factors were assigned to all other atoms. Hydrogen atoms were included in their geometrically calculated positions (C–H = 0.97 Å) with a single variable isotropic thermal parameter. The full-matrix least-squares refinement converged at $R = 0.041$ and $R_w = 0.039$ ($R = \sum|F_o| - |F_c|/\sum|F_o|$; $Rw = \sum w^{1/2}(||F_o| - F_c||)/\sum w^{1/2}|F_o|$; $w = 1.37/\sigma^2(F_o)$). The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$.[32] No systematic variation of $w(|F_o| - |F_c|)$ with $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The largest peak in the final difference map (1.2 e $Å^{-3}$) was located 0.95 Å from the Ir atom. The goodness-of-fit value ($[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$) was 1.59. All major calculations were performed on a VAX 6800 computer. Views of the molecule along with the atom-numbering scheme are shown in Figures 1 and 2, which were generated using ORTEP.[34] Final positional coordinates are given in Table II. Selected bond lengths and angles are presented in Table III. The supplementary material contains listings of thermal parameters and ligand geometries.

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Supplementary Material Available: Listings of bond distances and angles for the ligands and H atom positional parameters (4 pages). Ordering information is given on any current masthead page.

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Half-Open-Titanocene Chemistry: Coupling Reactions of Pentadienyl Ligands with Carbon–Nitrogen and Carbon–Oxygen Multiple Bonds

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The reactions of $Ti(C_5H_5)(2,4$-$C_7H_{11})(PEt_3)$ (C_7H_{11} = dimethylpentadienyl) with imines, ketones, and aryl isocyanides have been studied. In each case, the PEt_3 ligand is lost. In the reaction with benzylidenemethylamine, spectroscopic data indicate that coupling of the imine with one end of the 2,4-C_7H_{11} ligand has occurred. With acetone or 3-pentanone, 2 equiv is incorporated, leading to couplings with each end of the open dienyl ligand. A single-crystal X-ray diffraction study has been carried out for the latter. The space group is $P2_1/c$ with $a = 11.467$ (3) Å, $b = 7.647$ (2) Å, $c = 23.981$ (7) Å, $\beta = 92.11$ (3)°, and $V = 2101.3$ $Å^3$ for $Z = 4$. The structure was refined to discrepancy indices of $R = 0.042$ and $R_w = 0.042$ and revealed σ-allyl coordination as well as evidence for π-alkoxide donation. The reactions with RNC (R = C_6H_5, p-$CH_3C_6H_4$, p-$C_2H_5C_6H_4$) were found to lead to the incorporation of 4 equiv of RNC. In each case, two of the isocyanides have, with the pentadienyl ligand, formed a coordinated diazabutadiene ligand and a seven-carbon-atom ring, while the other two have formed an unusual indole which is attached to the former pentadienyl ligand and to an amide which is coordinated to the metal center. For the p-$C_2H_5C_6H_4NC$ product, the space group is $P\bar{1}$ with $a = 10.858$ (11) Å, $b = 11.103$ (5) Å, $c = 17.552$ (8) Å, $\alpha = 90.35$ (3)°, $\beta = 96.80$ (3)°, $\gamma = 104.28$ (6)°, and $V = 2034.8$ $Å^3$ for $Z = 2$. The structure was refined to discrepancy indices $R = 0.057$ and $R_w = 0.059$.

Metal pentadienyl compounds have proven to be very versatile in organometallic chemistry[3] and appear to offer particular promise for stoichiometric organic syntheses, whether through coupling reactions[4] or nucleophilic sub-

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stitutions,[5] as their cyclohexadienyl analogs already have.[6] Of particular interest to us are the half-open titanocenes, in which the pentadienyl ligand is more strongly bound than the cyclopentadienyl ligand, yet also more reactive, readily undergoing a coupling reaction with acetonitrile.[4b] Because of the relatively electropositive nature of titanium, a wide variety of related coupling reactions with other unsaturated organic compounds can be expected, as is indeed the case in analogous metal diene compounds.[7] Herein we report our results involving the coupling reactions of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ (C_7H_{11} = dimethylpentadienyl) with ketones, imines, and aryl isocyanides.

Experimental Section

All hydrocarbon, aromatic, and ethereal solvents were thoroughly dried and deoxygenated by distillation under nitrogen from Na/K benzophenone ketyl immediately before use. Deuterated benzene was degassed over potassium and stored in a glass bulb under nitrogen, while CD_2Cl_2 was dried over P_2O_5 under nitrogen. Infrared mulls were prepared in a glovebox with dry, degassed Nujol. All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen or in a glovebox. Solvents and solutions were added by glass syringes with stainless steel needles or by a pressure-equalizing addition funnel. Spectroscopic studies were carried out as previously described.[8] The ^{13}C NMR spectra were not integrated, but numbers of carbon atoms are provided with the resonances in accord with their assignments. Analytical data were obtained by Beller Laboratories and Oneida Research Laboratories. $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$[4b] and several aryl isocyanides[9] were prepared by literature procedures. Other organic compounds were obtained commercially.

$Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_6H_5NC)_4$. A 200-mL flask equipped with a magnetic stirring bar and nitrogen inlet was charged with 0.50 g (1.5 mmol) of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[P(C_2H_5)_3]$ and 20 mL of THF, resulting in an orange solution. Upon the addition of 0.98 mL of phenyl isocyanide (7.5 mmol) via syringe, a rapid color change from orange to dark red occurred. The resulting deep red solution was stirred for an additional 30–40 min, after which time the solvent was removed in vacuo, yielding a sticky red residue. Extraction of the residue with 100 mL of a 1:1 (v/v) mixture of hexanes and methylene chloride followed by filtration through a Celite and silica pad on a coarse frit gave a bright red solution. The filtrate was concentrated in vacuo while being heated until a sticky film began to form (ca. 20 mL total volume). Heating the solution to near boiling dissolved the film, and following slow cooling to room temperature over several hours, bright red crystals of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_6H_5NC)_4$ were formed. The supernatant was removed via syringe, and the crystals were dried in vacuo, yielding 0.63 g (67%) of the compound as virtually air-stable needles. ^1H NMR (C_6D_6, ambient): δ 7.60–6.65 (m, 19 H, phenyls), 6.51 (broad s, 1 H, N–H), 6.32 (s, 5 H, Cp), 4.47 (s, 1 H), 3.71 (d, 1 H, J = 15.4 Hz), 2.99 (d, 1 H, J = 13.6 Hz), 2.64 (d, 1 H, J = 16.1 Hz), 2.21 (d, 1 H, J = 13.5 Hz), 1.03 (s, 3 H, CH_3), 0.72 (s, 3 H, CH_3). ^{13}C NMR (C_6D_6, ambient): δ 153.4 (t, 1 C, J_{CN} = 8 Hz), 151.5 (t, 1 C, J_{CN} = 10 Hz), 151.2 (t, 1 C, J_{CN} = 9 Hz), 135.5 (s, 1 C), 134.3 (s, 2 C), 129.6 (d, 2 C, J = 158 Hz), 129.2 (d, 2 C, J = 159 Hz), 128.5 (d, 3 C, J = 158 Hz), 128.4 (d, 2 C, J = 158 Hz), 126.8 (d, 2 C, J = 159 Hz), 123.0 (d, 1 C, J = 159 Hz), 122.0 (d, 2 C, J = 153 Hz), 121.8 (d, 1 C, J = 153 Hz), 120.1 (s, 2 C), 119.8 (d, 1 C, J = 153 Hz), 119.4 (d, 1 C, J = 158 Hz), 117.3 (s, 1 C), 116.9 (s, 1 C), 116.7 (d, 2 C, J = 158 Hz), 11.6 (d of quintets, 5 C, J = 174, 6 Hz, Cp), 111.1 (d, 1 C, J = 158 Hz), 38.8 (s, 1 C), 33.8 (t, 1 C, J = 128 Hz), 32.4 (t, 1 C, J = 129 Hz), 27.7 (q, 1 C, J = 127 Hz), 27.6 (q, 1 C, J = 128 Hz). IR (Nujol mull): 3468 (m, sh), 2920 (vs, br), 1585 (s, sh), 1560 (m, shoulder), 1455 (vs, br), 1372 (s, sh), 1339 (m), 1298 (s, sh), 1260 (s, br), 1170 (w, sh), 1150 (m, sh), 1145 (m, shoulder), 1072 (m, sh), 1018 (m, sh), 987 (s, sh), 890 (m), 875 (m, sh), 812 (s, sh), 796 (s, sh), 750 (vs, sh), 740 (vs), 733 (vs, sh), 697 (m, sh), 689 (m), 670 (vw, br) cm^{-1}. Anal. Calcd for $C_{40}H_{36}N_4Ti$: C, 77.30; H, 5.84; N, 9.02. Found: C, 76.93; H, 5.83; N, 9.00.

$Ti(C_5H_5)(2,4\text{-}C_7H_{11})[4\text{-}CH_3(C_6H_4)NC]_4$. The complex $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[4\text{-}CH_3(C_6H_4)NC]_4$ was prepared in a manner identical with that for the phenyl isocyanide complex. Thus, the reaction of 0.50 g (1.5 mmol) of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[P(C_2H_5)_3]$ with 1.12 mL (7.5 mmol) of *p*-tolyl isocyanide resulted in the isolation of 0.63 g (62% yield) of the complex as bright red, air-stable needles that melt with no apparent decomposition at 301–303 °C. ^1H NMR (CD_2Cl_2, ambient): δ 7.13–6.65 (m, 15 H, phenyls), 6.50 (broad s, 1 H, N–H), 6.18 (s, 5 H, Cp), 4.60 (s, 1 H, H-3), 3.54 (d, 1 H, J = 16.1 Hz), 2.82 (d, 1 H, J = 13.5 Hz), 2.50 (d, 1 H, J = 16.1 Hz), 2.05 (d, 1 H, J = 13.2 Hz), 2.21 (s, 3 H, CH_3*), 2.04 (s, 3 H, CH_3*), 2.00 (s, 3 H, CH_3*), 1.87 (s, 3 H, CH_3*), 0.94 (s, 3 H, CH_3), 0.64 (s, 3 H, CH_3). ^{13}C NMR (CD_2Cl_2, ambient): δ 153.1 (t, 1 C, J_{NC} = 9 Hz), 149.0 (t, 1 C, J_{NC} = 14 Hz), 148.6 (t, 1 C, J_{NC} = 13 Hz), 135.9 (s, 1 C), 132.5 (s, 1 C), 132.2 (s, 2 C), 129.6 (s, 1 C), 129.4 (d, 1 C, J = 158 Hz), 128.8 (d, 2 C, J = 156 Hz), 128.6 (d, 3 C, J = 157 Hz), 128.6 (s, 1 C), 128.5 (d, 2 C, J = 155 Hz), 128.5 (d, 2 C, J = 158 Hz), 126.8 (s, 2 C), 124.6 (d, 1 C, J = 158 Hz), 123.0 (d, 1 C, J = 157 Hz), 121.7 (d, 1 C, J = 158 Hz), 119.2 (s, 2 C), 118.4 (d, 2 C, J = 155 Hz), 116.7 (s, 1 C), 111.0 (d of quintets, 5 C, J = 173, 6 Hz, Cp), 110.6 (d, 1 C, J = 160 Hz), 38.7 (s, 1 C), 33.4 (t, 1 C, J = 128 Hz), 32.1 (t, 1 C, J = 129 Hz), 28.0 (q, 1 C, J = 125 Hz), 27.2 (q, 1 C, J = 128 Hz), 21.4 (q, 1 C, J = 126 Hz), 20.5 (q, 1 C, J = 125 Hz), 20.4 (q, 1 C, J = 126 Hz), 20.1 (q, 1 C, 126 Hz). IR (Nujol mull): 3470 (m, sh), 3440 (m, sh), 2910 (vs, br), 1608 (s, sh), 1570 (w, sh), 1500 (vs, sh), 1465 (vs, br), 1374 (s), 1361 (s), 1347 (m), 1330 (s), 1297 (s), 1273 (s, sh), 1258 (m), 1229 (w, sh), 1187 (m, sh), 1170 (m), 1103 (w), 1087 (w), 1073 (w), 1056 (w), 1025 (s, sh), 958 (w), 941 (w), 902 (m, sh), 885 (s, sh), 875 (s), 868 (m, sh), 840 (s), 820 (s, sh), 807 (s), 795 (s), 783 (s), 745 (m), 720 (w), 708 (w, sh), 695 (w), 674 (w, sh) cm^{-1}. Mass spectrum (EI, 17 eV, 250 °C; m/z (relative intensity)): 678 (22), 677 (56), 676 (100), 675 (18), 674 (8), 479 (24), 478 (34), 57 (11). Anal. Calcd for $C_{44}H_{44}N_4Ti$: C, 78.09; H, 6.55; N, 8.28. Found: C, 77.80; H, 6.91; N, 8.10.

$Ti(C_5H_5)(2,4\text{-}C_7H_{11})[4\text{-}(C_2H_5)(C_6H_4)NC]_4$. In order to obtain single crystals of sufficient quality for an X-ray diffraction study, the 4-ethylphenyl isocyanide complex was also prepared. The procedure is similar to that used for the phenyl and *p*-tolyl isocyanide analogues with the exception of the extraction and crystallization steps. Thus, the addition of 1.1 mL (7.5 mmol) of 4-ethylphenyl isocyanide to 0.51 g (1.5 mmol) of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[P(C_2H_5)_3]$ in 30 mL of THF resulted in a dark red solution that gave a red oil following the removal of the THF in vacuo. The red oil was dissolved in 200 mL of hexanes, this solution was filtered through a Celite pad on a coarse frit, and the red filtrate was concentrated in vacuo to ca. 30 mL while hot until a film developed on the glass, at which point a reflux condenser was attached to the flask and the solution brought to a gentle reflux using a water bath. The film gradually dissolved (ca. 10 min), and the thermostatically controlled bath was cooled over 2 days, during which time dark red cubes of the product formed. The crystals so formed were found to be of sufficient quality for an X-ray diffraction analysis. Additional product was

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isolated by further concentration of the supernatant, resulting in a total of 0.82 g (75% yield) of dark red, essentially air-stable crystals. The crystals of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[4\text{-}(C_2H_5)(C_6H_4)NC]_4$ appear to be stable in air indefinitely and have a melting point of 298–301 °C. ^1H NMR (C_6D_6, ambient): δ 7.44 (s, 1 H, phenyl H), 7.3–7.1 (m, 13 H, phenyls), 7.05 (broad s, 1 H, N–H), 6.92 (s, 1 H, phenyl H), 6.47 (s, 5 H, Cp), 4.87 (s, 1 H, H-3), 3.83 (d, 1 H, J = 16.0 Hz), 3.10 (d, 1 H, J = 13.6 Hz), 2.84 (d, 1 H, J = 15.9 Hz), 2.78 (d, 1 H, J = 12.9 Hz), 2.77–2.51 (m, 8 H, Ph–CH_2CH_3), 1.17 (s, 3 H, CH_3), 0.86 (s, 3 H, CH_3), 1.33 (t, 3 H, J = 15.1 Hz, Ph–CH_2CH_3), 1.29 (t, 3 H, J = 14.0 Hz, Ph–CH_2CH_3), 1.23 (t, 3 H, J = 15.0 Hz, Ph–CH_2CH_3), 1.18 (t, 3 H, J = 14.0 Hz, Ph–CH_2CH_3). ^{13}C NMR (CD_2Cl_2, ambient): δ 153.9 (t, 1 C, J_{NC} = 8 Hz), 149.9 (t, 1 C, J_{NC} = 11 Hz), 149.6 (t, 1 C, J_{NC} = 10 Hz), 138.9 (s, 1 C), 138.8 (s, 1 C), 136.0 (s, 1 C), 135.8 (s, 1 C), 133.1 (s, 1 C), 132.2 (s, 1 C), 129.9 (s, 1 C), 129.2 (d, 2 C, J = 157 Hz), 128.8 (d, 4 C, J = 157 Hz), 122.6 (d, 2 C, J = 155 Hz), 122.2 (d, 4 C, J = 156 Hz), 120.0 (s, 2 C), 118.2 (d, 3 C, J = 155 Hz), 117.3 (s, 1 C), 117.2 (s, 1 C), 111.7 (d of quintets, 5 C, J = 172, 7 Hz, Cp), 111.1 (d, 1 C, J = 157 Hz), 39.1 (s, 1 C), 34.2 (t, 1 C, J = 130 Hz), 32.8 (t, 1 C, J = 132 Hz), 29.8 (t, 1 C, J = 125 Hz), 28.9 (t, 1 C, J = 126 Hz), 28.8 (t, 1 C, J = 125 Hz), 28.7 (t, 1 C, J = 125 Hz), 28.0 (q, 1 C, J = 126 Hz), 27.9 (q, 1 C, J = 126 Hz), 17.4 (q, 1 C, J = 125 Hz), 16.8 (q, 1 C, J = 125 Hz), 16.4 (q, 1 C, J = 125 Hz), 16.1 (q, 1 C, J = 125 Hz). IR (Nujol mull): 3475 (s, sh), 3020 (m, shoulder), 2960 (vs, br), 2860 (s, shoulder), 1895 (vw), 1865 (vw), 1604 (s), 1568 (w, sh), 1500 (vs), 1480 (s, shoulder), 1462 (s, br), 1452 (s), 1412 (m, shoulder), 1375 (s, sh), 1363 (s, sh), 1349 (m), 1334 (s), 1290 (vs, br), 1270 (s, shoulder), 1249 (m), 1185 (w, sh), 1171 (m, vsh), 1132 (m, sh), 1128 (m, shoulder), 1088 (w), 1060 (m), 1020 (m, sh), 1010 (m, sh), 957 (m), 935 (w), 918 (m), 899 (m), 887 (s, sh), 876 (s), 859 (w), 842 (s), 833 (s), 819 (vs), 807 (vs), 794 (vs), 768 (m), 750 (ms), 743 (ms, shoulder), 732 (m), 718 (m), 695 (m, sh), 674 (m, sh), 620 (ms) cm^{-1}. Mass spectrum (EI, 17 eV, 350 °C; m/z (relative intensity)): 732 (18), 551 (10), 537 (13), 523 (17), 368 (100), 313 (15), 264 (11), 239 (16), 237 (12), 236 (29), 129 (10), 121 (12), 112 (10), 106 (16), 98 (25), 97 (15), 95 (12), 85 (11), 84 (19), 73 (15), 71 (19), 60 (14), 57 (42), 56 (20), 55 (16). Anal. Calcd for $C_{48}H_{52}N_4Ti$: C, 78.74; H, 7.16; N, 7.65. Found: C, 78.58; H, 7.35; N, 7.15.

$Ti(C_5H_5)(2,4\text{-}C_7H_{11})[C_6H_5(H)N(CH_3)]$. Benzylidenemethylamine (0.12 mL, 0.98 mmol) was added via syringe to 0.32 g (0.98 mmol) of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[P(C_2H_5)_3]$ in 30 mL of THF at −78 °C. When the mixture was warmed, a rapid reaction (ca. 10 s) occurred at approximately −30 °C, as evidenced by a color change to deep red. No further changes were noted as the solution was warmed to room temperature and then stirred for an additional 12 h at this temperature. The solvent was removed in vacuo, leaving a dark red solid that was extracted with two 50-mL portions of pentane. The combined extracts were filtered through a Celite pad on a coarse frit, and the red filtrate was concentrated in vacuo to ca. 10 mL prior to cooling at −80 °C for 2 days. Removing the supernatant via syringe and drying in vacuo gave red/black cubes of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[C_6H_5(H)CN(CH_3)]$, mp 87–89 °C. It should be noted that the crystals of this compound become deliquescent at ca. 15 °C and bubbling of the resulting dark red oil is readily apparent; the "oil" then resolidifies into an amorphous glass after 2–3 h under a dynamic vacuum (ca. 10^{-3} Torr). This glasslike material (0.20 g, 62% yield) displays a sharp melting point, and analytical data are consistent with the formulation of the product as a 1:1 adduct of half-open titanocene and the imine. ^1H NMR (toluene-d_8, ambient): δ 7.2–7.0 (m, 5 H, phenyl H), 5.58 (s, 5 H, Cp), 4.24 (d, 1 H, J = 6.5 Hz, H_{5exo}), 3.79 (s, 1 H, H-3), 2.69 (d, 1 H, J = 6.5 Hz, H_{5endo}), 2.67 (s, 3 H, CH_3), 2.54 (d, 1 H, J = 7.2 Hz, H_{1exo}), 2.45 (d of d, 1 H, J = 14.3, 7.2 Hz, imine H), 2.14 (d, 1 H, J = 14.5 Hz, H_{1endo}), 1.63 (s, 6 H, CH_3). ^{13}C NMR (toluene-d_8, ambient): δ 129–128 (m, 6 C, Ph), 126.3 (s, 1 C, C-2 or C-4), 117.3 (d, 1 C, J = 152 Hz, C-3), 109.2 (d, 5 C, J = 171 Hz, Cp), 95.0 (s, 1 C, C-2 or C-4), 74.8 (d, 1 C, J = 132 Hz, C(H)N), 59.0 (t, 1 C, J = 151 Hz, C-5), 43.8 (t, 1 C, J = 129 Hz, C-1), 43.7 (q, 1 C, J = 132 Hz, $N(CH_3)$), 34.4 (q, 1 C, J = 128 Hz, CH_3), 30.1 (q, 1 C, J = 126 Hz, CH_3). IR (Nujol mull): 2910 (vs, br), 1595 (vw, br), 1455 (vs, br), 1408 (w, shoulder), 1373 (vs), 1332 (w, shoulder), 1270 (vw, br), 1258 (vw), 1208 (w), 1169 (w), 1151 (w, shoulder), 1107 (s, sh), 1068 (w), 1052 (w), 1022 (m, shoulder), 1010 (s, sh), 963 (m, sh), 875 (vw), 843 (w, br), 788 (vs, br), 758 (s, sh), 732 (s, shoulder), 718 (s, sh), 700 (vs, sh) cm^{-1}. Mass spectrum (EI, 17 eV; m/z (relative intensity)): 327 (6), 208 (66), 206 (100), 43 (12). Anal. Calcd for $C_{19}H_{25}NTi$: C, 73.39; H, 7.70; N, 4.28. Found: C, 73.08; H, 7.31; N, 4.31.

$Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_3H_6O)_2$. A clear orange solution of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})P(C_2H_5)_3$ (0.25 g, 0.77 mmol) in 30 mL of THF was cooled to −78 °C, and 0.12 mL (1.7 mmol) of acetone was added via syringe. The reaction mixture was warmed slowly while being stirred, and at ca. −30 °C the color quickly darkened to a deep red. The cold bath was removed and the reaction mixture stirred for an additional 12 h at room temperature, at the end of which time the solvent was removed in vacuo. Extraction of the resulting dark red solid with two 60-mL portions of pentane and filtration through a Celite pad on a coarse frit gave a dark red filtrate that was concentrated in vacuo to ca. 30 mL. The filtrate was cooled to −80 °C over 12 h, during which time red/black needles of the product formed. The supernatant was removed via syringe and the product, $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_3H_6O)_2$, dried in vacuo, yielding 0.14 g (0.44 mmol, 57% yield) of moderately air- and moisture-sensitive needles, mp 90–93 °C. ^1H NMR (benzene-d_6, ambient): δ 5.95 (s, 5 H, Cp), 4.48 (s, 1 H, H-3), 3.34 (d, 2 H, J = 13.8 Hz, $H_{1,5exo}$), 1.93 (s, 6 H, CH_3), 1.80 (d, 2 H, J = 13.5 Hz, $H_{1,5endo}$), 1.50 (s, 6 H, CH_3), 1.26 (s, 6 H, CH_3). ^{13}C NMR (benzene-d_6, ambient): δ 129.5 (d, 1 C, J = 153 Hz, C-3), 113.0 (d of quintets, 5 C, J = 172, 7 Hz, Cp), 100.8 (s, 2 C, C–O), 89.5 (s, 2 C, C-2,4), 48.4 (t, 2 C, J = 122 Hz, C-1,5), 33.6 (q, 2 C, J = 127 Hz, CH_3), 32.2 (q, 2 C, J = 124 Hz, CH_3), 31.5 (q, 2 C, J = 124 Hz, CH_3). IR (Nujol mull): 3098 (w, sh), 2920 (vs, br), 2720 (w, sh), 1540 (w, br), 1460 (vs), 1372 (s, sh), 1351 (s, sh), 1290 (w, sh), 1265 (m, sh), 1240 (m), 1211 (w), 1187 (m), 1160 (s, sh), 1149 (s, shoulder), 1121 (s), 1097 (s, sh), 1088 (w, sh), 1012 (s, vsh), 981 (s), 968 (s), 940 (s), 922 (s), 897 (s, sh), 842 (vw, sh), 799 (vs, sh), 775 (s, shoulder), 695 (w), 646 (s), 610 (s) cm^{-1}. Mass spectrum (EI, 17 eV, 100 °C; m/z (relative intensity)): 324 (3), 266 (12), 209 (10), 208 (100), 207 (14), 206 (88), 129 (11), 96 (13), 81 (13), 72 (33), 66 (41), 65 (11), 59 (89), 58 (34), 57 (65), 56 (13), 55 (15). Anal. Calcd for $C_{18}H_{28}TiO_2$: C, 66.66; H, 8.70. Found: C, 66.59; H, 8.83.

$Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_5H_{10}O)_2$. A clear solution of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})P(C_2H_5)_3$ (0.25 g, 0.77 mmol) in 50 mL of diethyl ether was cooled to −40 °C, and 0.18 mL (1.7 mmol) of 3-pentanone was added via syringe. The reaction mixture was warmed slowly while being stirred, and at ca. −30 °C the color deepened to a dark red. The cold bath was removed, and the reaction mixture was stirred an additional 1 h at room temperature. The solvent was then removed in vacuo. The resulting red solid was extracted with two 30-mL portions of pentane and filtered through a Celite pad on a coarse frit. The dark red filtrate was concentrated in vacuo to ca. 20 mL. The filtrate was then cooled to −80 °C over 12 h, during which time lumpy crystals were formed. The supernatant was removed via syringe, and the product was dried in vacuo, yielding 0.20 g (0.60 mmol, 37% yield) of moderately moisture- and air-sensitive crystals, mp 101.0–102.3 °C. These could be sublimed at 40 °C in vacuo to obtain crystals of sufficient quality for single-crystal X-ray diffraction studies. ^1H NMR (toluene-d_6, ambient): δ 5.94 (s, 5 H, Cp), 4.55 (s, 1 H, H-3), 3.14 (d, 2 H, J = 13.7 Hz, $H_{1,5exo}$), 1.91 (s, 6 H, CH_3), 1.88 (m, 2 H, $H_{1,5endo}$), 1.63 (d of q (pseudo sextuplet), 2 H, $J \approx 7$ Hz, CH_2), 1.47 (d of q (pseudo sextuplet), 2 H, $J \approx 7$ Hz, CH_2), 0.91 (q, 3 H, J = 7.2 Hz, CH_3), 0.84 (q, 3 H, J = 7.2 Hz, CH_3). ^{13}C NMR (benzene-d_6, ambient): δ 130.3 (d, 1 C, J = 116 Hz, C-3), 112.9 (d of quintets, 5 C, J = 172, 7 Hz, Cp), 112.4 (s, 2 C, C–O), 93.9 (s, 2 C, C-2,4), 45.2 (t, 2 C, J = 123 Hz, C-1,5), 33.7 (q, 2 C, J = 123 Hz, CH_3), 31.8 (t, 2 C, J = 125 Hz, CH_2), 31.5 (t, 2 C, J = 124 Hz, CH_2), 9.1 (q, 2 C, J = 127 Hz, CH_3), 9.0 (q, 2 C, J = 127 Hz, CH_3). Mass spectrum (EI, 70 eV, 80 °C; m/z (relative intensity)): 380 (2), 295 (11), 294 (25), 210 (17), 209 (34), 208 (100), 207 (36), 206 (87), 104 (11). Anal. Calcd for $C_{22}H_{36}TiO_2$: C, 69.48; H, 9.54. Found: C, 69.46; H, 9.59.

X-ray Data Collection for $CpTi(C_{17}H_{36}O_2)$. Crystal, data collection, and refinement parameters are collected in Table I. A well-shaped crystal, suitable for X-ray structure determination, was mounted on a fine glass fiber with epoxy cement. The unit cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic characterization showed $2/m$ Laue symmetry, and the systematic ab-

Table I. Crystallographic Data for CpTi($C_{17}H_{31}O_2$) and CpTi($C_{43}H_{47}N_4$)

	(a) Crystal Parameters	
formula	$C_{22}H_{36}O_2Ti$	$C_{48}H_{52}N_4Ti$
fw	380.41	732.85
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	11.467 (3)	10.858 (11)
b, Å	7.647 (2)	11.103 (5)
c, Å	23.981 (7)	17.552 (8)
α, deg	90	90.35 (3)
β, deg	92.11 (3)	96.80 (3)
γ, deg	90	104.28 (6)
V, Å^3	2101.3 (16)	2034.8 (25)
Z	4	2
cryst dimens, mm	0.30 × 0.32 × 0.32	0.26 × 0.32 × 0.37
cryst color	black	orange-red
D(calc), g/cm^3	1.202	1.062
μ(Mo Kα), cm^{-1}	4.27	2.50
temp, K	297	276
	(b) Data Collection	
diffractometer	Nicolet R3m	Nicolet R3
monochromator	graphite	graphite
radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
2θ scan range, deg	4–45	4–42
data collected (*hkl*)	±13, +9, +26	±11, ±11, 17
no. of rflns collected	3135	4555
no. of indpt rflns	2642	4282
no. of indpt obsd rflns, $F_o \geq n\sigma(F_o)$	2456 (n = 5)	2730 (n = 5)
std rflns	3 std/197 rflns	3 std/197 rflns
% var in stds	<2	<1
	(c) Refinement	
R(*F*), %	4.21	5.73
R(w*F*), %	4.22	5.90
Δ/σ(max)	0.051	0.04
Δ(ρ), e/Å^3	0.278	0.30
N_o/N_v	7.1	6.0
GOF	1.097	1.470

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for CpTiC$_{17}$H$_{31}$O$_2$

	x	*y*	*z*	*U*[a]
Ti	2183.9 (7)	8321.9 (12)	656.5 (4)	34.7 (3)
O(1)	637 (3)	8250 (4)	844 (1)	36 (1)
O(2)	2832 (3)	9490 (4)	1246 (1)	35 (1)
C(1)	1549 (5)	8203 (7)	−314 (2)	49 (2)
C(2)	1771 (4)	9918 (8)	−173 (2)	49 (2)
C(3)	2956 (5)	10111 (9)	−42 (2)	52 (2)
C(4)	3478 (4)	8488 (8)	−101 (2)	52 (2)
C(5)	2608 (5)	7290 (8)	−257 (2)	57 (2)
C(6)	372 (4)	7248 (6)	1334 (2)	34 (2)
C(7)	222 (4)	8495 (8)	1819 (2)	45 (2)
C(8)	−768 (8)	9777 (13)	1751 (4)	71 (3)
C(9)	−758 (4)	6260 (8)	1193 (2)	47 (2)
C(10)	−1213 (5)	5105 (9)	1639 (3)	70 (3)
C(11)	1436 (6)	6063 (10)	1457 (3)	40 (2)
C(12)	2128 (4)	5632 (7)	943 (2)	45 (2)
C(13)	1567 (5)	4194 (7)	589 (3)	59 (2)
C(14)	3393 (5)	5633 (7)	940 (2)	47 (2)
C(15)	4276 (5)	6489 (8)	1215 (2)	51 (2)
C(16)	5507 (5)	6183 (10)	1017 (3)	88 (3)
C(17)	4196 (4)	7646 (7)	1717 (2)	44 (2)
C(18)	3860 (4)	9549 (7)	1602 (2)	38 (2)
C(19)	3545 (5)	10444 (8)	2146 (2)	49 (2)
C(20)	3106 (6)	12290 (8)	2095 (3)	67 (2)
C(21)	4782 (5)	10577 (8)	1293 (3)	48 (2)
C(22)	5923 (5)	10901 (10)	1618 (3)	76 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances and Bond Angles for CpTi($C_{17}H_{31}O_2$)

	Bond Distances (Å)		
Ti–CNT[a]	2.072 (5)	Ti–O(1)	1.846 (3)
Ti–O(2)	1.809 (3)	Ti–C(14)	2.558 (6)
Ti–C(12)	2.170 (6)	O(2)–C(18)	1.430 (6)
O(1)–C(6)	1.444 (6)	C(6)–C(11)	1.539 (8)
C(11)–C(12)	1.527 (8)	C(12)–C(14)	1.451 (7)
C(14)–C(15)	1.355 (8)	C(15)–C(17)	1.500 (8)
C(17)–C(18)	1.529 (8)	C(12)–C(13)	1.517 (8)
C(15)–C(16)	1.524 (8)		
	Bond Angles (deg)		
CNT–Ti–O(1)	115.4 (2)	CNT–Ti–O(2)	126.3 (2)
CNT–Ti–C(12)	118.7 (2)	CNT–Ti–C(14)	107.2 (2)
O(1)–Ti–O(2)	101.2 (1)	O(1)–Ti–C(12)	81.7 (2)
O(1)–Ti–C(14)	115.3 (2)	O(2)–Ti–C(12)	103.7 (2)
O(2)–Ti–C(14)	89.2 (2)	C(12)–Ti–C(14)	34.5 (2)
Ti–O(1)–C(6)	116.5 (3)	Ti–O(2)–C(18)	142.0 (3)
Ti–C(12)–C(11)	94.2 (4)	Ti–C(12)–C(13)	121.8 (4)
Ti–C(12)–C(14)	87.5 (3)	Ti–C(14)–C(12)	57.9 (3)
Ti–C(14)–C(15)	97.4 (4)	O(1)–C(6)–C(11)	106.2 (4)
C(6)–C(11)–C(12)	113.8 (5)	C(11)–C(12)–C(14)	123.5 (5)
C(11)–C(12)–C(13)	112.7 (5)	C(13)–C(12)–C(14)	113.7 (5)
C(12)–C(14)–C(15)	136.7 (5)	C(14)–C(15)–C(16)	117.3 (5)
C(14)–C(15)–C(17)	127.4 (5)	C(16)–C(15)–C(17)	115.1 (5)
O(1)–C(6)–C(7)	108.8 (4)	O(1)–C(6)–C(9)	106.6 (4)
O(1)–C(6)–C(11)	106.2 (4)	O(2)–C(18)–C(17)	105.9 (4)
O(2)–C(18)–C(19)	108.0 (4)	O(2)–C(18)–C(21)	107.3 (4)

[a] CNT = centroid of atoms C(1)–C(5).

sences in the diffraction data uniquely established the space group as $P2_1/c$. An absorption correction was not applied to the data set (low μ, T_{max}/T_{min} = 1.062).

Structure Solution and Refinement. The structure was solved by direct methods, which located the Ti atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier and least-squares syntheses. All hydrogen atoms, except those on carbon atoms C(13) and C(16), were found and refined isotropically. The hydrogen atoms on carbon atoms C(13) and C(16) were included as idealized isotropic contributions (d(CH) = 0.960 Å, U = 1.2U(attached C)). All non-hydrogen atoms were refined with anisotropic thermal parameters. Table II contains positional parameters, and Table III contains relevant bond distances and bond angles.

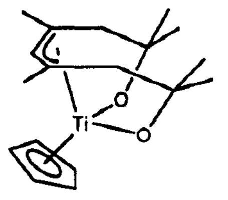
All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (version 5.1, by G. Sheldrick, Nicolet (Siemens), Madison, WI).

X-ray Data Collection for CpTi($C_{43}H_{47}N_4$). An orange-red crystal was mounted on a glass fiber and found to possess $\bar{1}$ Laue symmetry. The centrosymmetric space group $P\bar{1}$ was initially selected on the basis of its frequency of occurrence; this selection was confirmed by the chemically reasonable results of refinement. The maximum 2θ for data collection was limited to 42°, at which point only 5% of the reflections were observed. No correction for absorption was required.

Structure Solution and Refinement. The structure was solved by direct methods and expanded by a series of difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were placed in idealized locations. All computations used SHELXTL (version 5.1) software written for the (Nicolet) Siemens Corp., Madison, WI, by G. Sheldrick.

Results and Discussion

The half-open titanocene Ti(C_5H_5)(2,4-C_7H_{11})(PEt$_3$) reacts readily with ketones R_2CO (R = CH_3, C_2H_5), benzylidenemethylamine ($C_6H_5C(H)NCH_3$), and various aryl isocyanides (RNC, R = C_6H_5, p-$CH_3C_6H_4$, p-$C_2H_5C_6H_4$). In the reaction of Ti(C_5H_5)(2,4-C_7H_{11})(PEt$_3$) with ketones, 2 equiv of the latter is readily incorporated, yielding apparently symmetric products by room-temperature ^{1}H and ^{13}C NMR spectroscopy (i.e., mirror-plane symmetry is retained) of the stoichiometry Ti(C_5H_5)(2,4-C_7H_{11})(R_2CO)$_2$ (R = CH_3, C_2H_5). That these compounds are not simple ligand adducts is revealed by the ^{13}C–H coupling constants of ca. 122 Hz for the pentadienyl CH$_2$ groups, clearly indicating formal sp^3 hybridization. This would likely result from their coupling to the ketones, yielding products such as I, reminiscent of related reactions which occur between early-metal butadiene compounds and ketones.[7]



I

A single-crystal X-ray diffraction study has been carried out to better define the structure of this coupling product. Pertinent bonding parameters are presented in Tables II and III, while the structure is depicted in Figure 1. It can readily be seen that the general structure does correspond to that of I, except that a σ, rather than π, allyl–Ti interaction is observed, which then removes the mirror plane of symmetry. The σ nature of this interaction is clearly revealed by the relative Ti–C(12,14,15) distances 2.170 (6), 2.558 (6), and 3.046 (7) Å compared to an average Ti–C bond distance of 2.385 (10) Å for the C_5H_5 ligand.[10] For comparison, the corresponding σ- and π-bond distances for $Ti(C_5H_5)_2[C_4(C_6H_5)_4]$[11] are 2.156 (4) and 2.386 (7) Å, and those for $Ti(C_5H_5)_2[(C_5H_4)Mn(CO)_3]_2$[12] are 2.207 (2) and 2.396 (6) Å, respectively. For $Ti(C_5H_5)_2(\eta^1\text{-}C_5H_5)_2$,[13] the Ti–C σ-bond length is longer still, being 2.332 (2) Å. The σ-allyl formulation is further indicated by the respective C(12)–C(14) and C(14)–C(15) bond lengths of 1.451 (7) and 1.355 (8) Å. Of course, the presence of a σ-allyl linkage should remove the apparent mirror-plane symmetry observed in the room-temperature NMR spectra. However, even at a temperature of −80 °C, decoalescence is not observed, although there might be some line broadening. Thus, the apparent mirror-plane symmetry must be the result of a very facile rearrangement, in which the Ti–C(12) bond is broken and replaced by a Ti–C(15) bond. It would seem most likely that this rearrangement would involve an intermediate π-allyl complex.[14]

The nature of the alkoxide–Ti interactions, however, requires closer inspection. If the interaction were purely σ in nature, the titanium center would only achieve a 12-electron configuration, somewhat unusual given the presence of a σ-allyl ligand. In fact, however, there is good reason to expect that significant π alkoxide–Ti interactions take place. Thus, although the covalent radius of oxygen is only 0.11 Å less than that of carbon,[15] the π Ti–O bonds are ca. 0.32–0.36 Å shorter than the Ti–C(12) bond and reasonably similar to the Ti–O distance of 1.855 (2) Å in $Ti(C_5H_5)(OC_2H_5)Cl$.[16] While the Ti–O–C bond angles are likely to be constrained somewhat by the chelating nature of the coupled organic linkage, they do also provide some further evidence of an interaction. The Ti–O(1)–C(6) angle of 116.5 (3)° reveals some expansion relative to formal sp^3 hybridization, although it has opened up neither to the extent expected for sp^2 hybridization (120°) nor to the extent observed in $Ti(C_5H_5)_2(OC_2H_5)Cl$ (133.2 (2)°). However, there is no observable difference between these two Ti–O bond lengths (*d*(Ti–O(1) = 1.846 (3) Å vs 1.855 (2) Å), perhaps a reflection of the greater potential electron deficiency in our compound. On the other hand, the Ti–O(2)–C(18) angle has expanded all the way to 142.0 (3)° and is accompanied by the shortest Ti–O bond, 1.809 (3) Å. It seems at least possible that partial π donation to titanium is also occurring from the second lone pair of electrons on O(2).[17] In such a hybrid, the alkoxide ligand would function as a 5-electron donor. Counting the other alkoxide as a 3-electron donor would then lead to an 18-electron configuration for titanium. Of course, the chelating nature of the coupled ligand complicates the interpretation of the bonding and perhaps even retards the extent of π donation from the alkoxide ligands. However, judging from the large deviation of the Ti–O(2)–C(18) angle from 180°, and the fact that 16-electron titanium complexes are not uncommon[4b,18] (e.g., the imine and perhaps isocyanide coupling products, vide infra), it seems that the 16-electron assignment, in which both alkoxides serve as 3-electron donors, would be more reasonable.[19]

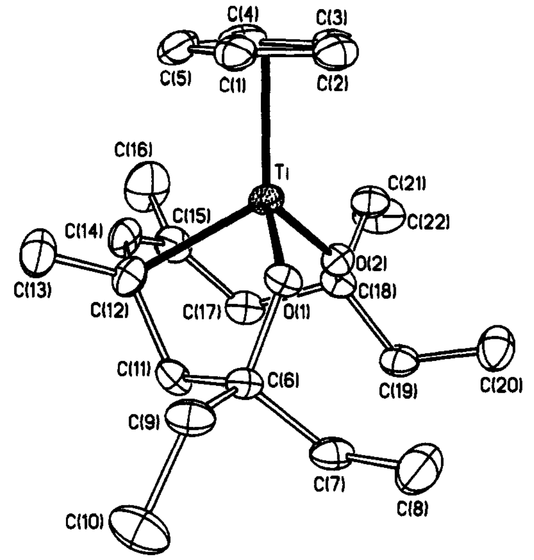


Figure 1. ORTEP drawing of $CpTi(C_{17}H_{31}O_2)$. Ellipsoids are drawn at 35% probability. Hydrogens are omitted for clarity.

In the case of the imine reaction, a 1:1 stoichiometry is followed, as was earlier found for the related reaction with CH_3CN,[4b] which led to a dimeric product, II, through the formation of a Ti_2N_2 ring. The imine reaction could have proceeded quite analogously, leading to the dimeric product III, in which the carbon–nitrogen double bonds

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(10) Avarage values for $M–C(C_5H_5)$ distances are provided with esd's for the mean value, based upon the distribution of the individual values (not on the individual esd's). Averages based on smaller numbers of data are presented with the esd for the mean values, derived from the individual esd's.

(11) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* 1976, *98*, 2454.

(12) Daroda, R. J.; Wilkinson, G.; Hursthouse, M. B.; Abdul Malik, K. M.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* 1980, 2315.

(13) Calderon, J. L.; Cotton, F. A.; DeBoer, B. G.; Takats, J. *J. Am. Chem. Soc.* 1971, *93*, 3592.

(14) Although the apparent 16-electron configuration for the σ-allyl complex would not necessitate a loss in π-alkoxide interactions for the π-allyl intermediate, there could be an extra π-alkoxide component (vide infra) which would be lost, and changes in geometric constraints could have further effects.

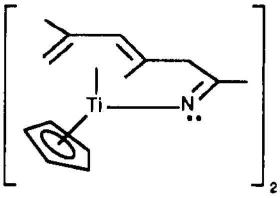
(15) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(16) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* 1980, *102*, 3009.

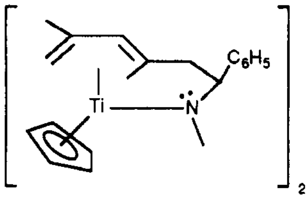
(17) (a) In the analysis of the structure of $Ti(C_5H_5)_2(OC_2H_5)Cl$,[16] it was concluded that a Ti–O–C angle of 133° represents an energy minimum for an alkoxide ligand serving as a 3-electron donor. The fact that the angle about O(2) (instead of O(1)) is closer to this value is consistent with the relative Ti–O bond distances here, although additional π donation by O(2) may also contribute. (b) There is good evidence that significant distortion is brought about within the ligand backbone in order to achieve effective coordination. Many of the angles about various carbon atoms appear unusual relative to their formal sp^2 or sp^3 hybridizations: C(6)–C(11)–C(12) = 113.8 (5)°, Ti–C(12)–C(11) = 94.2 (4)°, Ti–C(12)–C(14) = 87.5 (3)°, C(12)–C(14)–C(15) = 136.7 (5)°, C(14)–C(15)–C(17) = 127.4 (5)°, C(15)–C(17)–C(18) = 116.0 (4)°. This may be the result of an attempt to open the Ti–O–C angles for optimal π overlap.

(18) (a) Bottrill, M.; Gavens, P. D.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; p 281. (b) Bottrill, M.; Gavens, P. D.; Kelland, J. W.; McMeeking, J. In ref 18a, pp 331, 433. (c) Ernst, R. D.; Liu, J.-Z.; Wilson, D. R. *J. Organomet. Chem.* 1983, *250*, 257.

(19) For comparison, in $[Ti(C_5H_5)Cl_2]_2O_2C_2(CH_3)_4$,[16] a Ti–O–C bond angle of 166.2 (2)° and a Ti–O distance of 1.750 (2) Å were observed.

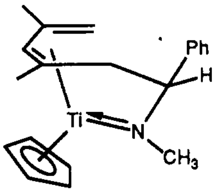


II



III

are replaced by single bonds. Thus, the ^{13}C NMR spectra demonstrate that one of the terminal CH_2 groups from the pentadienyl ligand is now formally sp^3 hybridized ($J(^{13}C{-}H)$ = 129 Hz), while the other is still formally sp^2 hybridized ($J(^{13}C{-}H)$ = 151 Hz). There is no direct spectroscopic evidence to indicate that the pentadienyl fragment has rearranged to the sickle conformation, but that formulation would be preferred by analogy to the structural result for II. However, as opposed to the case for II, it would be possible for the imine product to be monomeric and for the nitrogen atom to function as a 3-electron donor through a π interaction with the titanium center as in IV. In either the proposed monomeric or dimeric structures, a 16-electron configuration would result for titanium.[20]



IV

In contrast to the results for nitrile and imine couplings, the behavior of aryl isocyanides is quite different. Even with a 1:1 ratio of isocyanide to titanium complex, the isolated products contain 4 equiv of isocyanide. Of course, the yields are low based on titanium, but in reactions with higher ratios of isocyanides, much better yields may be obtained. While the incorporation and coupling of 4 equiv of isocyanide have also been observed on reaction with $Zr(CH_3C_5H_4)_2H_2$,[21] the pentadienyl ligand in this case would not be expected to behave innocently, and indeed ^{13}C NMR spectroscopy provided some important clues in this regard. First, the NMR spectroscopic data indicated that no symmetry was present in the product molecules since the two sides of a given pentadienyl fragment were nonequivalent, as were all aryl groups. Extensive coupling of the isocyanides could be inferred from the infrared spectrum, which displayed no free C=N or C≡N stretching modes but did contain clear N—H and C=C bands. That the pentadienyl ligands were involved in the couplings was apparent from the $J(^{13}C{-}H)$ values of 128–132 Hz observed for the terminal CH_2 groups of the various products. Little else could be deduced from the spectroscopic data, and resort to X-ray diffraction was made for structural assignment. While all of the isocyanides examined were found to provide spectroscopically analogous products, in general they were not isolated as single crystals. However, the use of *p*-ethylphenyl isocyanide did lead to a product which more readily provided single crystals.

Table IV. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $CpTiC_{43}H_{47}N_4$

	x	*y*	*z*	*U*[a]
Ti	8301.3 (10)	3318.8 (9)	7969.9 (8)	46.8 (4)
N(1)	9282 (4)	2389 (4)	7412 (2)	42 (2)
N(2)	9758 (4)	93 (4)	8824 (2)	51 (2)
N(3)	7426 (4)	2306 (4)	8735 (2)	45 (2)
N(4)	6654 (4)	3119 (4)	7350 (2)	49 (2)
C(1)	8183 (6)	5383 (5)	8284 (4)	69 (3)
C(2)	9020 (7)	5457 (5)	7721 (4)	73 (3)
C(3)	10074 (7)	5048 (5)	8044 (4)	73 (3)
C(4)	9897 (7)	4720 (5)	8791 (4)	69 (3)
C(5)	8744 (8)	4943 (5)	8949 (3)	68 (3)
C(6)	6332 (5)	1837 (5)	7469 (3)	49 (2)
C(7)	5811 (6)	920 (5)	6788 (3)	58 (3)
C(8)	6745 (6)	238 (5)	6544 (3)	55 (3)
C(9)	7540 (6)	−235 (5)	6988 (3)	53 (2)
C(10)	7730 (5)	−324 (5)	7874 (3)	47 (2)
C(11)	6690 (5)	82 (5)	8260 (3)	47 (2)
C(12)	6717 (5)	1437 (4)	8174 (3)	42 (2)
C(13)	6754 (7)	174 (6)	5687 (3)	83 (3)
C(14)	7630 (6)	−1700 (5)	8045 (3)	64 (3)
C(15)	9043 (5)	473 (5)	8188 (3)	43 (2)
C(16)	10896 (5)	1002 (5)	8986 (3)	47 (2)
C(17)	11916 (6)	1041 (6)	9553 (3)	60 (3)
C(18)	12959 (7)	2033 (7)	9570 (3)	65 (3)
C(19)	13049 (6)	2969 (6)	9029 (3)	63 (3)
C(20)	12018 (6)	2904 (5)	8480 (3)	54 (3)
C(21)	10930 (6)	1933 (5)	8455 (3)	45 (2)
C(22)	9723 (5)	1607 (4)	7966 (3)	40 (2)
C(23)	14281 (7)	3996 (6)	9057 (4)	96 (4)
C(24)	14162 (8)	5205 (7)	8770 (5)	121 (4)
C(25)	9713 (5)	2448 (5)	6696 (3)	46 (2)
C(26)	10485 (5)	1720 (5)	6464 (3)	58 (3)
C(27)	10854 (6)	1795 (6)	5739 (4)	74 (3)
C(28)	10483 (7)	2611 (7)	5206 (3)	77 (3)
C(29)	9715 (6)	3332 (6)	5439 (3)	71 (3)
C(30)	9331 (6)	3254 (5)	6160 (3)	57 (3)
C(31)	10909 (8)	2718 (8)	4403 (4)	107 (4)
C(32)	9974 (9)	1982 (9)	3842 (5)	136 (6)
C(33)	7421 (5)	2075 (5)	9522 (3)	42 (2)
C(34)	8558 (6)	2375 (5)	10023 (3)	51 (3)
C(35)	8535 (6)	2237 (5)	10810 (3)	56 (3)
C(36)	7397 (7)	1759 (5)	11107 (3)	63 (3)
C(37)	6284 (6)	1439 (5)	10599 (3)	61 (3)
C(38)	6289 (5)	1596 (5)	9824 (3)	54 (2)
C(39)	7366 (7)	1638 (6)	11972 (3)	85 (3)
C(40)	7350 (8)	360 (7)	12225 (4)	110 (4)
C(41)	5799 (5)	3706 (5)	6914 (3)	51 (2)
C(42)	6266 (6)	4678 (6)	6463 (4)	74 (3)
C(43)	5460 (6)	5336 (7)	6081 (4)	86 (3)
C(44)	4165 (6)	5020 (6)	6128 (4)	73 (3)
C(45)	3706 (6)	4035 (6)	6555 (4)	77 (3)
C(46)	4493 (6)	3359 (6)	6941 (3)	62 (3)
C(47)	3291 (7)	5765 (7)	5744 (4)	104 (4)
C(48)	3534 (11)	7011 (10)	6035 (7)	243 (9)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The solid-state structure of the *p*-ethylphenyl isocyanide coupling product is depicted in Figure 2, and pertinent bonding parameters are contained in Tables IV and V. As had been surmised from spectroscopic data, both ends of the pentadienyl ligand had coupled and become incorporated into a seven-membered ring with the terminal carbon atoms of two isocyanides. A third isocyanide, whose fate will be discussed more fully later, has also coupled to the pentadienyl ligand (at the 2-position), thereby converting it to a neutral and uncoordinated olefin. The first two isocyanides have thus been converted to a diazabutadiene fragment which is bonded in an η^4 fashion to the titanium center. As is often the case for butadiene complexes of low-valent early transition metals,[7,22] one can observe that the terminal (in this case, nitrogen) atoms are significantly closer (ca. 0.4 Å) to the metal center. The Ti–C(6) and Ti–C(12) bond lengths (averaging 2.418 (4) Å) are slightly

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[20] An isopiestic molecular weight determination was inconclusive, perhaps the result of a monomer ⇄ dimer equilibrium.

[21] Bocarsly, J. R.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1986**, *5*, 2380.

[22] (a) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008. (b) Melendez, E.; Arif, A. M.; Rheingold, A. L.; Ernst, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 8703.

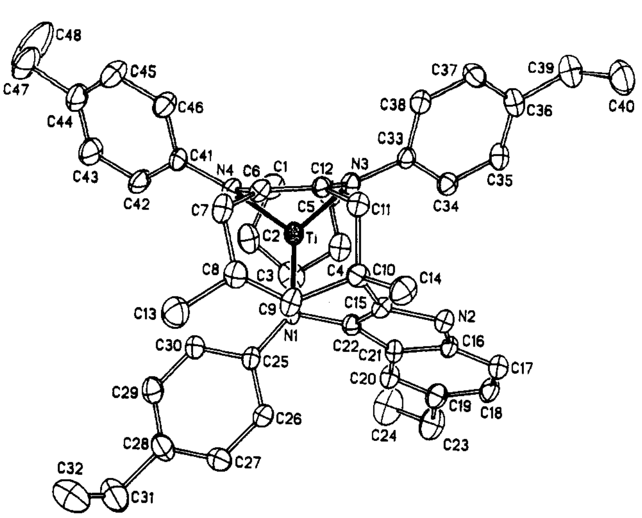
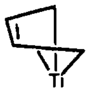


Figure 2. ORTEP drawing of CpTi($C_{43}H_{47}N_4$). Ellipsoids are drawn at 35% probability. Hydrogens are omitted for clarity, as are the bonds from Ti to C(6) and C(12).

Table V. Selected Bond Distances and Bond Angles for CpTi$C_{43}H_{47}N_4$

	Bond Distances (Å)		
Ti–N(1)	1.983 (5)	Ti–C(1)	2.391 (6)
Ti–N(3)	1.941 (4)	Ti–C(2)	2.370 (6)
Ti–N(4)	1.942 (4)	Ti–C(3)	2.350 (6)
Ti–C(6)	2.420 (5)	Ti–C(4)	2.357 (6)
Ti–C(12)	2.416 (5)	Ti–C(5)	2.404 (6)
N(1)–C(22)	1.426 (7)	N(3)–C(12)	1.392 (6)
N(1)–C(25)	1.388 (7)	N(3)–C(33)	1.407 (6)
N(2)–C(15)	1.410 (7)	N(4)–C(6)	1.402 (7)
N(2)–C(16)	1.387 (6)	N(4)–C(41)	1.418 (8)
C(6)–C(7)	1.525 (7)	C(1)–C(2)	1.409 (10)
C(6)–C(12)	1.371 (7)	C(1)–C(5)	1.400 (9)
C(7)–C(8)	1.505 (10)	C(2)–C(3)	1.395 (11)
C(8)–C(9)	1.302 (9)	C(3)–C(4)	1.386 (10)
C(8)–C(13)	1.507 (8)	C(4)–C(5)	1.393 (12)
C(9)–C(10)	1.551 (7)	C(10)–C(15)	1.518 (7)
C(10)–C(11)	1.538 (9)	C(15)–C(22)	1.377 (7)
C(10)–C(14)	1.538 (8)	C(16)–C(21)	1.392 (8)
C(11)–C(12)	1.506 (7)	C(21)–C(22)	1.442 (7)
	Bond Angles (deg)		
N(1)–Ti–N(3)	111.2 (2)	N(4)–C(6)–C(7)	119.9 (4)
N(1)–Ti–N(4)	106.4 (2)	N(4)–C(6)–C(12)	118.0 (4)
N(3)–Ti–N(4)	88.5 (2)	C(7)–C(6)–C(12)	120.9 (5)
Ti–N(1)–C(22)	105.2 (3)	C(6)–C(7)–C(8)	114.9 (5)
Ti–N(1)–C(25)	135.6 (4)	C(7)–C(8)–C(9)	127.2 (5)
Ti–N(3)–C(12)	91.4 (3)	C(7)–C(8)–C(13)	113.4 (5)
Ti–N(3)–C(33)	145.7 (3)	C(9)–C(8)–C(13)	119.4 (6)
Ti–N(4)–C(6)	91.3 (3)	C(8)–C(9)–C(10)	130.7 (6)
Ti–N(4)–C(41)	146.9 (3)	C(9)–C(10)–C(11)	112.5 (5)
C(22)–N(1)–C(25)	118.7 (5)	C(9)–C(10)–C(14)	107.0 (4)
C(15)–N(2)–C(16)	107.6 (4)	C(9)–C(10)–C(15)	109.1 (4)
C(12)–N(3)–C(33)	121.6 (4)	C(11)–C(10)–C(14)	107.7 (4)
C(6)–N(4)–C(41)	121.8 (4)	C(11)–C(10)–C(15)	109.9 (4)
N(2)–C(15)–C(10)	120.4 (4)	C(14)–C(10)–C(15)	110.6 (5)
N(2)–C(15)–C(22)	108.9 (4)	C(10)–C(11)–C(12)	113.7 (4)
C(10)–C(15)–C(22)	130.7 (5)	N(3)–C(12)–C(6)	119.2 (4)
N(2)–C(16)–C(21)	109.3 (5)	N(3)–C(12)–C(11)	119.6 (4)
C(16)–C(21)–C(22)	106.7 (4)	C(6)–C(12)–C(11)	119.1 (4)
N(1)–C(22)–C(15)	126.9 (4)	C(15)–C(22)–C(21)	107.5 (4)
N(1)–C(22)–C(21)	125.3 (4)		

longer than the average Ti–C(Cp) distance of 2.374 (10) Å.[10] For the butadiene complexes, one observes in such cases a long–short–long backbone, and a bonding picture such as in V is deemed appropriate. Particularly notable, then, is the observation that the diazabutadiene fragment also exhibits a long–short–long backbone, despite the smaller size of nitrogen relative to carbon atoms, which could be attributed to a similar resonance hybrid such as VI. In fact, the average C–N distance of 1.397 (5) Å is quite similar to the C–N single-bond distances in the rest of the structure (average 1.406 (3) Å), while the C(6)–C(12) bond distance of 1.371 (7) Å is somewhat longer than the uncoordinated C(8)–C(9) olefinic bond (1.302 (9) Å) but much shorter than the other formal single bonds in the seven-membered ring, which range from 1.505 (10) to 1.551 (7) Å. It can be noted that, in other early-metal complexes, the coordination pattern has been found to range from the extreme represented by VI to that expected for VII.[23]



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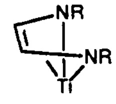
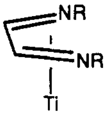
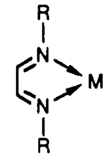


VI

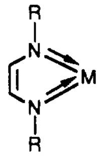


VII



VIII

However, late-metal 1,4-diazabutadiene complexes generally can be considered to display coordination through the nitrogen lone pairs of the neutral molecule (VIII).[24] Interestingly, a closer examination of some of the bonding parameters suggests that the situation here is still more complex. In particular, both N(3) and N(4) possess nearly trigonal-planar coordination geometries, with their respective sums of subtended angles being 358.7 and 360.0°.[25] This allows for the possibility that these atoms could each be serving as 3-electron donors by virtue of a resonance hybrid such as IX. Thus, the diazabutadiene ligand may actually be considered to serve as an overall 6-electron donor. The fact that the Ti–N(3) and Ti–N(4) bonds are shorter than the Ti–N(1) bond (in which nitrogen also serves as a 3-electron donor, vide infra) is in accord with this possibility. A similarity between IX and some bis(carbene) complexes may be noted.[26]



IX

The third isocyanide ligand has coupled to the 2-position (C(10)) of the former pentadienyl ligand, converting it into a neutral olefin molecule. It has also coupled to the fourth isocyanide ligand, leading to an indole fragment and a coordinated amide group. The indole appears normal, with the C–C bonds in the six-membered ring ranging from 1.369 (9) to 1.406 (9) Å, and a shorter C(15)–C(22) bond relative to the C(21)–C(22) bond (1.377 (7) vs 1.442 (7) Å). The coordinated amide nitrogen atom is essentially sp^2 hybridized, with Ti–N(1)–C(22), Ti–N(1)–C(25), and C(22)–N(1)–C(25) bond angles of 105.2 (3), 135.6 (4), and

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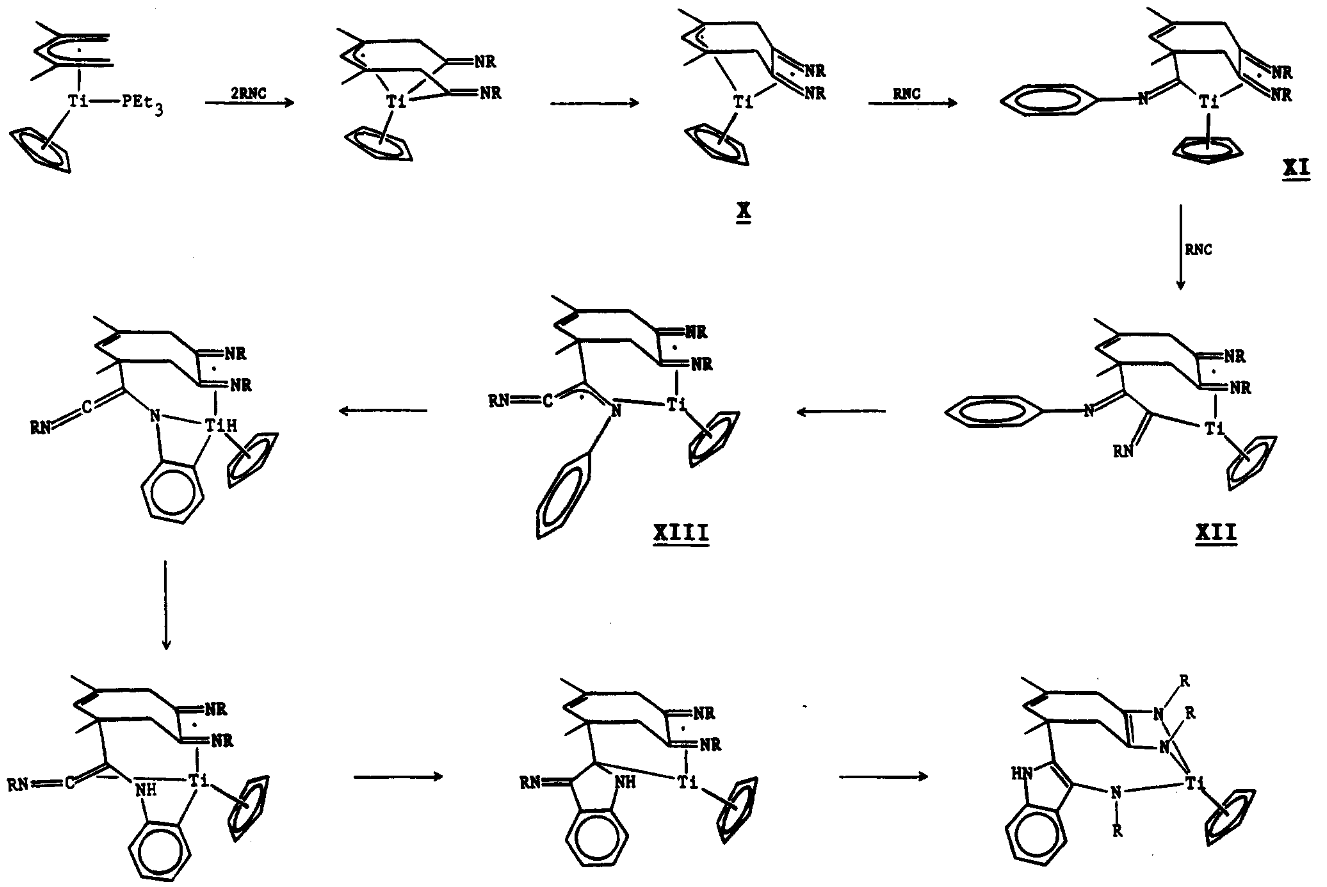
(23) (a) Erker, G. Private communication. (b) Hessen, B.; Bol, J. E.; de Boer, J. L.; Meetsma, A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1989**, 1276. (c) Woitha, C.; Behrens, U.; Vergopoulos, V.; Rehder, D. *J. Organomet. Chem.* **1990**, *393*, 97.

(24) (a) Svoboda, M.; tom Dieck, H.; Krüger, C.; Tsay, Y.-H. *Z. Naturforsch.* **1981**, *36B*, 814. (b) Gross, M. E.; Ibers, J. A.; Trogler, W. C. *Organometallics* **1982**, *1*, 530. (c) Trogler, W. C. *Acc. Chem. Res.* **1990**, *23*, 426.

(25) However, the titanium atom does not lie in the plane of the diazadiene ligand as a result of the tilts of 33.5 and 36.6°, respectively, between the diazabutadiene and Ti–N(3)–C(12)–C(33) and Ti–N(4)–C(6)–C(41) planes.

(26) Albers, M. O.; de Wall, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680.

Scheme I



118.7 (5)°, respectively (sum 359.5°). Thus, this nitrogen atom can be regarded as donating 3 electrons to the titanium center, leading to either a 16- or 18-electron configuration, depending on how the diazabutadiene coordination is viewed (vide supra). The fact that the Ti–N(1) bond length of 1.983 (5) Å is actually longer than the Ti–N(3) and Ti–N(4) bonds could be a result of the attachment of the indole fragment to the former pentadienyl unit, which may not allow for optimal approach of N(1) to the titanium center. In fact, the observed asymmetry of the Ti–N–C(22,25) and C(10)–C(15)–(C(22),N(2)) bond angles may also be a result of this attachment.

With the structure of the isocyanide complexes now established, the mechanism by which they were formed becomes of interest. While one could suggest a number of potential mechanisms for these reactions, recognition of some important characteristics of the pentadienyl ligands suggests the general mechanism outlined in Scheme I to be especially plausible. In particular, while couplings between isocyanide ligands have been observed in other systems,[27] the great steric demands of the pentadienyl ligands, and their high proclivity in these systems to undergo coupling reactions,[28] render it much more likely that stepwise initial coordinations of the first two isocyanides are each quickly followed by coupling, or migratory insertion, reactions to an end of the pentadienyl fragment.[29] It is also very unlikely that the coupling to the formally uncharged C-2 position (labeled C(10) in Figure 2) would occur first, both due to its additional two-carbon-atom attachments and to the clear precedents with ketone, imine, and nitrile ligands, in which only couplings to the terminal pentadienyl carbon atoms occur.[4b] Once the two isocyanide ligands have coupled to the ends of the pentadienyl ligand (Scheme I),[30] a formal reductive elimination can lead to the diazabutadiene complex X, which bears some similarity in its backbone structure to the ketone coupling products (vide supra) but due to its cyclic nature could quite easily be expected to encounter significant difficulties in achieving effective binding to both the allylic (whether σ or π) and diazabutadiene fragments. In fact, the closeness of the titanium atom to the nitrogen atoms of the final product's diazabutadiene fragment and the resulting orientation of titanium away from the allylic portion of the pentadienyl fragment (Figure 2) provide compelling support for such expected difficulties. The intermediate X would therefore be expected to be quite susceptible to the incorporation of an additional isocyanide molecule, whose subsequent coupling to the allyl fragment

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[27] (a) Filippou, A. C.; Grüleitner, W. *J. Organomet. Chem.* **1990**, *393*, C10. (b) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 6987. (c) Bianconi, P. A.; Vrtis, R. N.; Rao, Ch. P.; Williams, I. D.; Engeler, M. P.; Lippard S. J. *Organometallics* **1987**, *6*, 1968.

[28] (a) While isocyanide complexes of (pentadienyl)chromium compounds may be isolated,[28b] the greater oxophilicity of titanium may lead to a greater driving force for the coupling reaction. It is possible, and we have some reason to suspect, that some of the titanium reactions may actually involve electron-transfer steps. (b) Freeman, J. W.; Hallinan, N.; Arif, A. M.; Gedridge, R. W.; Ernst, R. D.; Basolo, F. *J. Am. Chem. Soc.* **1991**, *113*, 6509.

[29] (a) Although Ti(C_5H_5)(2,4-C_7H_{11})(CO)$_2$ can be isolated, it is only stable under a CO atmosphere and is in equilibrium with the 16-electron monocarbonyl.[29b] Thus, while the formation of an 18-electron bis(isocyanide) complex is not inconceivable, it appears more likely that the predominant and participating form is the 16-electron mono(isocyanide) complex. (b) Waldman, T. E. Ph.D. Dissertation, University of Utah, 1990.

[30] (a) While Scheme I depicts the two RNC ligands each coupling separately to the dienyl ends prior to coupling to themselves, it is also possible that, upon coordination, the second isocyanide couples first to the other, already coupled, isocyanide and then to the other dienyl end. Stepwise couplings of two isocyanides to a butadiene ligand have also been proposed.[30b] (b) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 830.

would seem quite plausible, if not inevitable. While the foregoing steps seem relatively clear, on the basis of previous pentadienyl chemistry, the driving forces for the following steps are not as readily apparent. Intermediate XI still contains a Ti–C single bond, perhaps quite strained, and could again be susceptible to a coordination and coupling of a fourth isocyanide molecule, resulting in an iminoacyl complex[31] which can most easily be represented by XII, although the actual coordination is likely to be more complex (possibly dynamic), as in XIII. Subsequent ortho-metalation, hydride-transfer, and coupling steps would lead to the observed product. While it would be possible to have the ortho metalation precede the coordination of the fourth isocyanide ligand, this alternative is not favored here, though by no means ruled out, as one might expect the ortho-metalation step to require a greater energy of activation than an additional coordination and migratory insertion involving the fourth isocyanide, particularly given the possibility that the bonding of the third isocyanide in XI might still be strained.

The facility with which (pentadienyl)titanium compounds undergo coupling reactions with unsaturated organic molecules such as nitriles, isonitriles, imines, ketones, and acetylenes demonstrates that a rich body of chemistry in this area remains to be explored. It can be expected that some of these reactions will prove useful for the syntheses of organic molecules, particularly if some control can be exerted on the number of incorporated unsaturated molecules.[32] Such a possibility seems likely, and efforts utilizing highly substituted cyclopentadienyl ligands are currently underway.

Registry No. $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[P(C_2H_5)_3]$, 116841-88-4; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[4\text{-}(C_2H_5)(C_6H_4)NC]_4$, 143063-90-5; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_5H_{10}O)_2$, 143063-91-6; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_6H_5NC)_4$, 143063-92-7; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[4\text{-}CH_3(C_6H_4)NC]_4$, 143063-93-8; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[C_6H_5(H)N(CH_3)]$, 143063-94-9; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_3H_6O)_2$, 143063-95-0; phenyl isocyanide, 931-54-4; *p*-tolyl isocyanide, 7175-47-5; 4-ethylphenyl isocyanide, 143063-89-2; benzylidenemethylamine, 622-29-7; acetone, 67-64-1; 3-pentanone, 96-22-0.

Supplementary Material Available: Tables of complete bond distances, bond angles, anisotropic thermal parameters, and positional parameters of hydrogen atoms (10 pages). Ordering information is given on any current masthead page.

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[31] (a) Iminoacyl and related species are not uncommon results of insertion reactions.[31b,c] (b) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4063 and references therein. (c) Beshouri, S. M.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 2375 and references therein.

[32] (a) Synthetic routes to new indole systems are of interest,[32b,c] although the ones obtainable herein are certainly quite specialized. (b) Tidwell, J. H.; Senn, D. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 4685. (c) Alvarez, M.; Salas, M.; Joule, J. A. *Heterocycles* **1991**, *32*, 1391.

Synthesis and X-ray Structural Characterization of $Mg(2,4,6\text{-}R_3C_6H_2)_2(THF)_2$ (R = Me, *i*-Pr) and the Three-Coordinate Magnesiate Species $[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$

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Addition of 1,4-dioxane to a tetrahydrofuran solution of $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)MgBr$ results in the disproportionation of the Grignard reagent to give $MgBr_2$–dioxane and the bulky diorganomagnesium compound $Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$. Further reaction with $[Li(Et_2O)(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]_2$ yields the magnesiate species $[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$. Each compound has been structurally and spectroscopically characterized by X-ray crystallography and ^1H NMR. We also report the X-ray crystal structure of the known species $Mg(Mes)_2(THF)_2(Mes = 2,4,6\text{-}Me_3C_6H_2\text{-})$. $[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$ is the first unassociated lithium organomagnesiate compound involving a structure with three-coordinate magnesium. Crystal data at 130 K with Mo Kα ($\lambda = 0.71069$ Å) radiation are as follows: $Mg(Mes)_2(THF)_2$, orthorhombic, $a = 9.019$ (2) Å, $b = 28.752$ (6) Å, $c = 36.782$ (6) Å, $Z = 16$, space group $F2dd$, $R = 0.045$; $Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$, orthorhombic, $a = 33.865$ (10) Å, $b = 33.912$ (11) Å, $c = 12.406$ (4) Å, $Z = 16$, space group $Fdd2$, $R = 0.040$; $[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$, monoclinic, $a = 12.819$ (3) Å, $b = 15.103$ (3) Å, $c = 24.500$ (5) Å, $\beta = 91.13$ (2)°, $Z = 4$, space group $P2_1/c$, $R = 0.080$.

Organic derivatives of magnesium are among the most common organometallic synthetic reagents.[1] Generally, they are categorized as either Grignard reagents or diorganomagnesium compounds which can be represented by the formulas RMgX and MgR_2, respectively (R = alkyl, aryl; X = halide). These descriptions are misleading since two-coordinate magnesium is unknown at room temperature in the donor solvents in which they are synthesized. In addition, their existence in solution is characterized by equilibria 1 and 2. These equilibria are often complicated

$$2RMgX \xrightleftharpoons{\text{solvating medium}} MgR_2 + MgX_2 \qquad (1)$$

$$2R_2Mg \xrightleftharpoons{\text{solvating medium}} MgR^+ + MgR_3^- \qquad (2)$$

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[1] (a) Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds*, 3rd ed.; Methuen: London, 1967. (b) Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 1, Chapter 4. (c) Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F. *Adv. Organomet. Chem.* **1991**, *32*, 147.

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